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13. ABSTRACT (Maximum 200 words)

Wide temperature, solid lubricant films offer payoffs for military turbomachinery components: rub seals, face seals, fretting interfaces and bearings. Multilayer films of B_4C/Mo, B_4C/Cr, Zn/W, Ni/Ti, Au/Cr, W/MoS and AlCuFeCr films were deposited by planar magnetron sputtering or ion bombardment assisted deposition (IBAD), and evaluated for adhesion, friction and wear properties from room temperature to as high as 1100°F. Oxidized Zn/W and W/MoS_2 films exhibited low friction coefficients at room temperature . However, only AlFeCuCr quasicrystalline films consistently produced low friction coefficients at high temperature, suggesting that these films warrant further investigation. High friction coefficients obtained with IBAD Ni-Ti films at 1100°F were especially puzzling given previous Southwest Research Institute results that showed low friction values at high temperature.

14. SUBJECT TERMS

Ion beam, magnetron sputtering, solid lubricants, high temperature, bearings, fretting

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Ion Beam Deposited Metal Oxide and Fluoride Composite Coatings for High Temperature Tribological Applications

Phase I SBIR

Contract No: F49620-97-C-0056

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I. OBJECTIVES

The primary objective of this Phase I program was to identify and demonstrate stable, wear resistant nano-composite and/or multilayer thin films which exhibit wide temperature lubricity capabilities up to temperatures as high as 850°C. Coatings deposited by both magnetron sputtering and ion assisted deposition were deposited and evaluated in an effort to discover one or more promising material systems.

II. EXPERIMENTAL RESULTS

II.1 Definition Of Operational Requirements For Near-Term and Next Generation Gas Turbine Engines-Select Coatings Materials And Coating Architectures.

Anti-Seizing Lubricant Problem for Turbine Engine Fasteners

The principal objective of this task was to define realistic opportunities for the military and spin-off commercial applications of advanced wide temperature solid lubricants. Based on discussions with Pratt and Whitney (P&W), General Electric (GE) and, in particular, Oklahoma City Air Logistics Center (OC-ALC) engineering personnel, one of the best opportunities, is for anti-seize-solid lubricant compounds to prevent seizing and fretting in gas turbine engine components. Present anti-seize compounds are ineffective above 900°F. Seizing of fasteners costs the AF and Department of Defense (DoD) millions of dollars annually in scrapped parts and additional maintenance time. Some details help highlight the extent of this dilemma. Collectively, fielded TF-30, F110 and F-100 engines, as well as the F119 engine for the new F22 fighter, have more than 5000 fasteners exposed to temperatures greater than 850°F. The F119 engine has more than 1600 fasteners that operate at 850°F or higher. It is estimated that the fastener seizing problem costs all the services 25 million dollars plus per year in replacement and repair.

Using P&W's F-100 engine as a specific example is instructive. Approximately 20% of the F100 engine hot section bolts are discarded at disassembly due to excessive torques that cause cracking or shearing of the bolts. A savings of $2.4 M in life cycle costs could be achieved for the F100-PW-220 engine if an improved anti-seize compound were available. Silver plating, which is presently the primary high temperature anti-seize material, has several liabilities. First, it increases the cost of a fastener by ten percent. Secondly, silver is susceptible to corrosion, limiting the coating to fastener threads only. Silver can react with sulfur and chlorides present in turbine combustor gases causing stress induced corrosion of titanium-based, nickel-based and cobalt-

based alloys. For the same reasons, silver plating cannot be used with MoS_2 or lead-containing solid lubricants. Specific examples of high temperature fastener problems, particularly with silver plating in different AF engines, is illustrated in Table 1.

Table 1. Turbine Engine Anti-Seize Problems (Examples)

•F-100, Stress corrosion in EGV Bolts due to reaction of 586 on bolts with a silver plated clinch nut (bolt Waspaloy).
Fuel nozzle corrosion due to galvanic action between silver plated bolt & 347 stainless flange.
•PW229, 13th bld lock set screw seizing, break down of 586 due to heat and oxidation. (While attempting to remove the lock the drum rotor was damaged $$).
•TF30, afterburner fuel manifold nut stress corrosion, silver plating on stainless 347 nut.
2nd Turbine Vane lock bolt lead embrittlement from FELPRO C200 or Stress Corrosion from interaction of C200 and silver.
•JT9D, 1st Stage Turbine Airseal keywasher fracture, stress corrosion due to interaction of C200 and silver.
•GE F110, HPT disk cracks due to silver plated nuts and bolts reacting with sulfur in fuel.

Several different anti-seize compounds are used throughout these turbine engines causing an additional logistics burden and additional storage requirements and multiple stock numbers. For example, the F100 engine uses five different lubricants.

The GE F110 engine which, in addition to P&W's F-100, is also used to power the Air Force F-16 and F-15 aircraft also has a serious need for an improved anti-seize compound. In fact, OC-ALC has provided a list of hot section areas and specific fasteners that need an improved high temperature anti-seize compound. These fasteners and their locations are listed in Table 2.

In summary, there is a significant payoff for a single anti-seize (solid lubricant) compound for fasteners exposed to temperatures of 850°F and higher. Therefore, one of the goals of this STTR effort was to develop, qualify and implement a solid lubricant/anti-seize compound that would be inexpensive, non-corrosive, environmentally safe, and effective to at least 1250°F and applicable to all gas turbine engines. Such a lubricant will become increasingly important as the Air Force and other military services introduce hotter, higher thrust-to-weight engines into future aircraft systems.

Table 2. F110 Fasteners Requiring High Temperature Anti-Seize Compounds

Aft Centerbody		Nut plate -J1100P04A and B Bolt - J334P08A 1360M21P01 9132M23P04
HPT Forward Shaft		Aft Bolt - 9514M87P02 Aft Nut - 9514M87P02 9528M69P05
HPT Inner Nozzle Support		Fwd nut - 1441M48G01 - 1441M49G01 (nut assy) Fwd bolt - 992M17P02 Aft nut - 9232M90P07 and P09 Aft bolt - J334P13A
Inner Aft Support		Aft bolt -1385M79P01 Aft nut - 9943M62G03 - nut assy. J1051P03A and B Mid bolt - 1498M37P01 Mid nut - 9943M62G03 - nut assy. J1051P03
HPT disk		Aft bolt - 1275M34G01 Aft nut - 9528M39P04

TA&T has compiled a list of requirements for developing and qualifying anti-seize coatings for turbine engine fasteners. These include lab scale screening tests, assembly and breakaway torque tests as a function of temperature, reusability testing, corrosion/testing and bolt elongation testing. TA&T has also contacted the Aerospace Products Division of SPS Technologies, Inc. about participating in a phase II program, assuming that the phase I effort is successful and that phase II is funded. This division of SPS Technologies, the largest supplier of aerospace fasteners, agreed to conduct the fastener MIL-SPEC tests; i.e. torque-tension, salt fog, corrosion etc. Mr. Mike Colandonato is the point-of-contact for SPS Technologies. Mr. Aaron Larsen, Chief of Acquisition Engineering Section at OC-ALC, agreed to help qualify these coatings once successful MIL-SPEC test results have been achieved.

Details on the problems and need for improved anti-fretting coatings for turbine-blade root areas of turbine engines were provided in the phase I proposal and will not be repeated here. Additional applications such as start up-touchdown coatings for gas bearing turbomachinery and other gas bearing devices were also addressed in the proposal.

II.2 Initial Coating Deposition And Friction and Wear Results

One of the major concepts for this Phase 1 effort was to find multilayer material combinations in the as-deposited condition that would convert to useful solid lubricants under in-service oxidizing conditions. These were classified "as adaptive solid lubricants."

TA&T's and SwRI's respective work on magnetron sputtered B_4C/Mo and IBAD Ni/Ti films, which suggested that these coatings could be lubricious at high temperatures, served as a starting point. In addition, B_4C/Cr, Ti/B_4C, CaF_2/Ag, and BCN IBAD films were deposited by SwRI. TA&T concentrated on the magnetron sputtered Zn/W multilayer system. Previous work on pulsed laser deposition of WS_2/ZnO dual layer coatings by Dr. Jeff Zabinski's group at the Materials and Manufacturing Directorate at Wright Patterson AFB, Ohio had shown that WS_2/ZnO dual layer coatings reacted in high temperature air to form a lubricious $ZnWO_4$ coating. Ultra-thin Zn/W multilayers were expected to react in a similar fashion. In addition, the Wear Sciences and Coatings Group (WSCG) of TA&T also deposited NiCr/Zn, B_4C/Mo, Ag/MoS_2 multilayers, B_4C/MoS_2 dual layers, B_4C/Mo multilayers + BN top coat and B_4C with dispersed island Ag/MoS_2 multilayers. The specific sputtering parameters used for each experimental sputtered coating (target power, carousel rotation speed) is given in Table 3.

II.3 Magnetron Sputtered Films and Room Temperature Friction and Wear Results

The coefficient of friction (COF) and wear test results of W/Zn multilayer, single layer B_4C, dual layer B_4C+MoS_2, B_4C/Mo multilayer, BrC/Mo multilayer + BN topcoat and Ag/MoS_2 multilayer films are also summarized in Table 3. The room temperature COF results of two as-deposited W/Zn disks from WT# 27 and WT # 28 were 0.11 and 0.31, respectively. While these as-deposited COF values were encouraging, the results from a W/Zn specimen from the same batch that was annealed at 300°C in air for one hour was even more encouraging. It was predicted that this metallic multilayer system should form an adaptive lubricious oxide coating. The COF plots for the as-deposited W/Zn film (WT#27) and the annealed at 300°C in air for one hour W/Zn film are shown in Figure 1a and 1b, respectively. The low (0.1) COF and small 52100 ball wear scar (0.15 mm) and disk wear track width (0.25mm) suggested that a lubricious $ZnWO_4$ had formed. Subsequent X-ray diffraction analyses revealed the presence of a mixed $ZnWO_4+WO_3$ phase, which supported this assumption. All coated disks were loaded against a 52100 steel or WC ball at a Hertzian stress of 1.1 and 1.3 GPa and rotated at 670 rpm.

II.4 Other Sputtered Films - Room Temperature Friction and Wear Results

The COF and wear results of the other films in Table 3 showed that oxidized NiCr/Zn multilayer films exhibited higher COF values than W/Zn films but comparatively small wear scars (WT# 60) under very high stress of 3.4 GPa. However, the lowest room temperature COF values were obtained with a B_4C film that was annealed in moist air at 100°C for one hour (WT#174), a B_4C film with a MoS_2 top coat (WT # 176), a B_4C/Mo multilayer with a BN top coat (WT# 199) and a Ag/MoS_2 multilayer film (WT#42). These low COF results were attributable to the formation of a thin, low friction, boric acid layer on B_4C as previously shown by Edemir, and low shear strength solid lubricants in the case of the MoS_2, BN and Ag/MoS_2. The beneficial effect of the H_3BO_3 layer on B_4C is dramatically displayed by comparing the COF plot of Figure 2a with the as-sputtered B_4C COF plot in Figure 2b.

The next step in this initial screening series was to determine if any of these combinations exhibited reasonable COFs in a high temperature oxidizing environment. These tests were conducted at SwRI. The results are described in the next section.

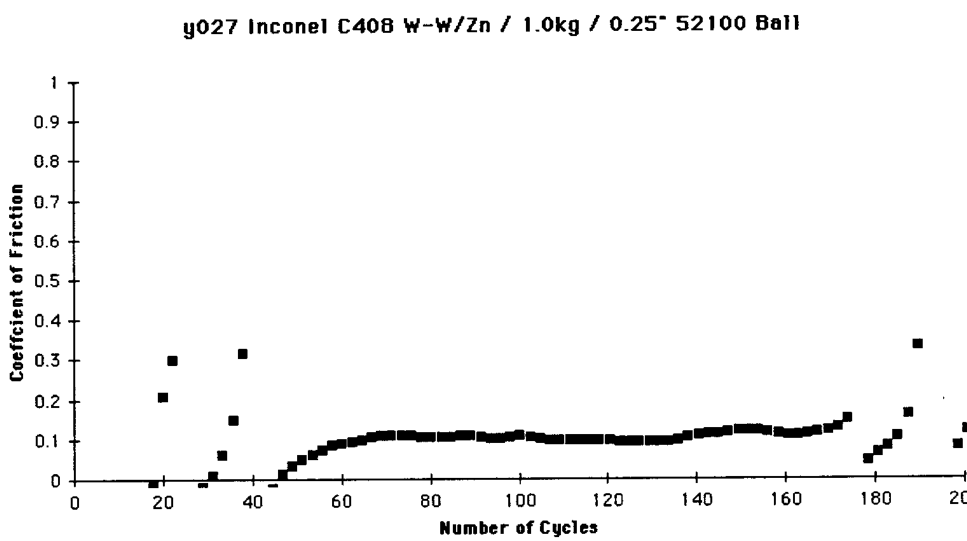

Figure 1a. Coefficient of friction of 2μm thick as-sputtered W/Zn multilayer film at 670 RPM under a 1.3 GPa load.

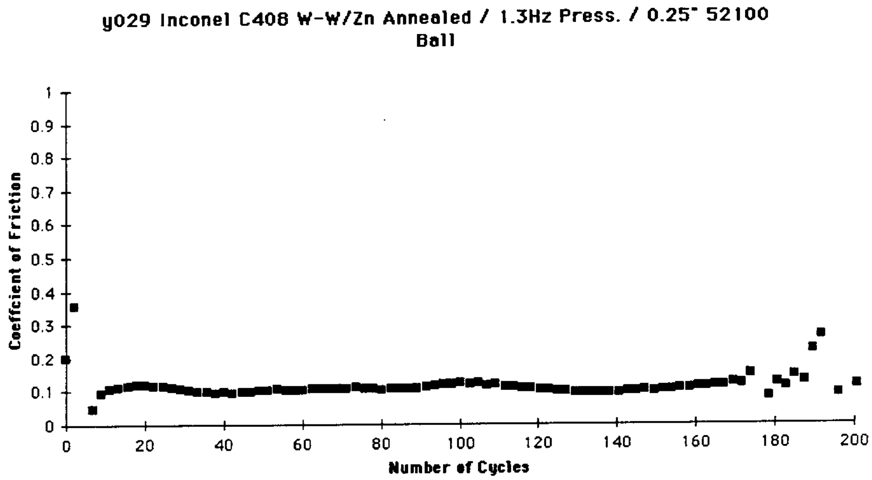

Figure 1b. Coefficient of friction of 2μm thick annealed (300°C, 1 HR) sputter W/Zn multilayer film at 670 RPM under a 1.3 GPa load.

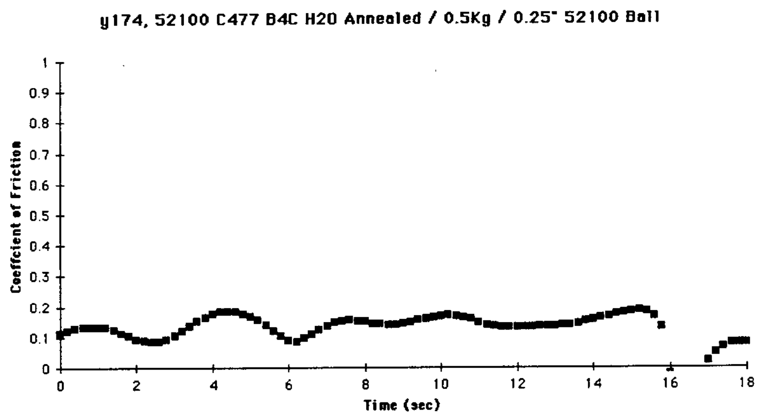

Figure 2a. Coefficient of friction of 100°C-1 Hr annealed sputtered B_4C film at 670 RPM under 1.1 GPa load.

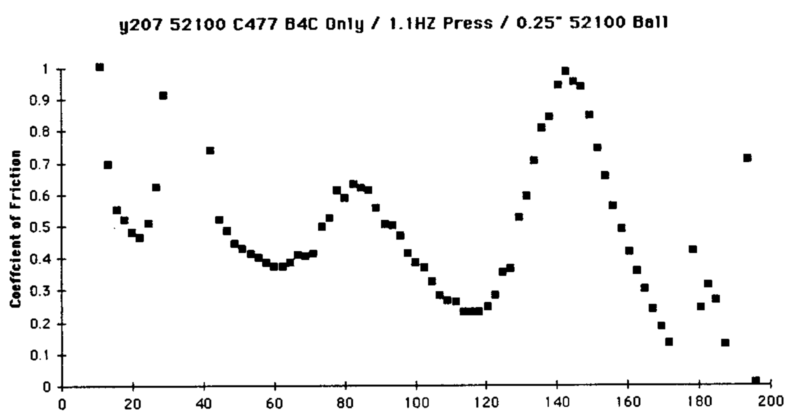

Figure 2b. Coefficient of friction of as-sputtered B_4C film at 670 RPM under a 1.1 GPa load.

II.5 IBAD Ni/Ti Films and Room Temperature Friction and Wear Results

The first set of IBAD experiments was based on the Ni/Ti system. SwRI coated four Inconel disks provided by TA&T. The first two IBAD coatings were dual layer Ni/Ti coatings approximately 200 nm in total thickness. These were subjected to high energy 80 KeV Ar^+ and N_2^+ ion beam mixing, respectively, similar to coatings deposited by Lankford and co-workers at SwRI several years ago. The other two Inconel disks were used for SwRI's first attempts at IBAD multilayer coatings. One was a 20 layer film Ni/Ti with 100nm bilayer periodicity (2μm total thickness) deposited under 2 KeV Ar^+ bombardment and the other was a 20 layer film with 150 nm bilayer periodicity (3μm total thickness) deposited under a 2 KeV N_2^+ ion beam. These IBAD coated disks were shipped to TA&T for room temperature pin-on-rotating disk tests. The disks were loaded against a 52100 steel ball at a Hertzian stress of either 1.3 or 1.1 GPa and rotated at 670 RPM. The COF and wear scar results of these four Ni/Ti films are shown in Table 3 (wear test numbers 65,54, 56 and 189).

The 80 KeV N_2^+ ion beam mixed, dual layer thin film exhibited the lowest COF (average of 0.1 in wear test # 65) followed by the low energy 2 KeV N_2^+ ion beam assist Ni/Ti multilayer 2 μm thick film (WT #189). The COF plots for these films are shown in Figure 3a and 3b, respectively. Both the Ar^+ ion beam mixed dual layer (WT# 54) and Ar^+ IBAD Ni/Ti multilayer (WT# 56) exhibited high COFs of 0.4 and 0.55, respectively. The excessively high COF plot of the Ar^+ ion beam mixed dual layer Ni/Ti film is presented in Figure 4. The formation of a thin TiN surface layer under N_2^+ bombardment probably accounts for the lower COF of the N_2^+ bombarded films versus the Ar^+ bombarded Ni/Ti films. Auger electron spectroscopy (AES) analysis of the surface and sputter depth spectroscopy profiling of these Ni/Ti films confirmed the presence of the TiN phase.

II.6 Other IBAD Experimental Films-Room Temperature Friction and Wear Results

An initial survey of other IBAD coatings provided to TA&T for room temperature pin-on-disk testing included:

(a) 2 μm B_4C with a thin Ti bond layer (α 0.15 μm) using 2keV Ar ion assist and an identical B_4C film with an N_2^+ assist.

(b) a 3 μm CaF_2/Ag multilayer film with a 150 nm periodicity using 2 KeV N_2^+ assist;

c) a 3 μm B_4C/Cr multilayer with 150 nm periodicity using a 2 KeV N_2^+ assist. This film consisted of 21 layers with a Cr layer being deposited first and last.

The wear test numbers and results for these IBAD coatings are shown in Table 3 in order of list above: WT # 188, #186, #187 and #185. None of these coatings exhibited COFs as low as the target goal of 0.2. All these coatings appeared to suffer from adhesion problems since the COF values of all these coatings increased abruptly immediately after start-up or just a few seconds into the test. TA&T recommended that SwRI implement longer ion beam etch similar to TA&T's procedure in order to assure that the substrates are extremely clean prior to starting the IBAD coating process.

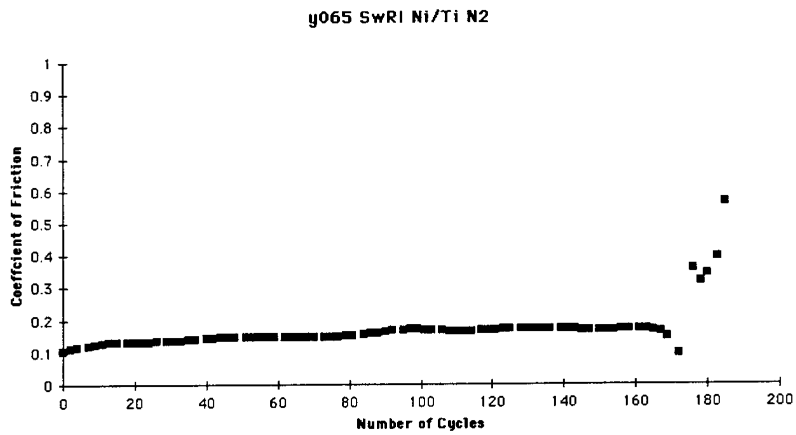

Figure 3a. Coefficient of friction of 0.2μm thick 80 KeV N_2^+Ni/Ti dual layer film at 670 RPM under 1.3 GPa load.

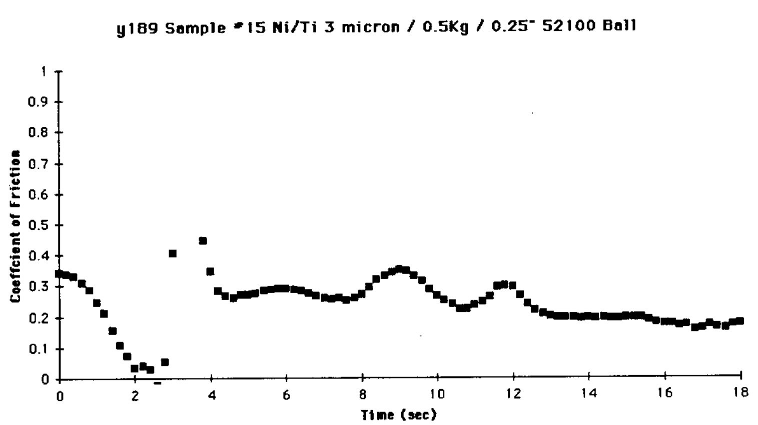

Figure 3b. Coefficient of friction of 2μm thick, 2 KeV N_2^+ Ni/Ti multilayer film with 100 nm periodicity at 670 RPM under 1.1 GPa load.

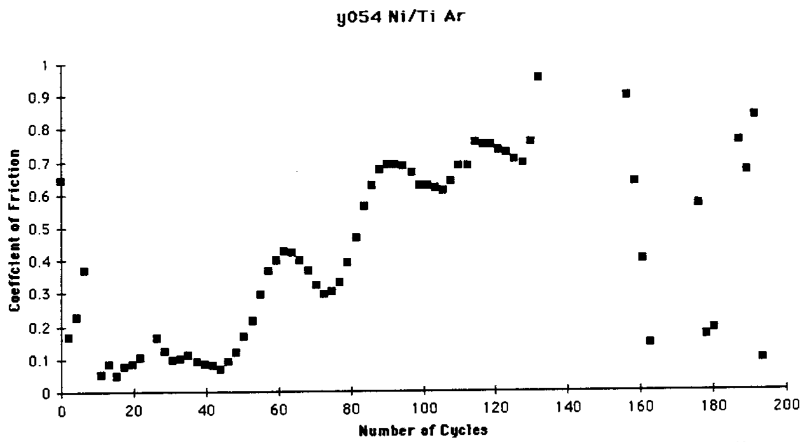

Figure 4. Coefficient of friction of 0.2μm thick 80 KeV N_2^+Ni/Ti dual layer film at 670 RPM under a 1.3 GPa load.

Table 3 Room Temperature COF DATA For IBAD and Magnetron Sputtered Lubricant Films

Wear Test No	Coating No	Coating Materials	Coating condition	Substrate	Treatment	Ball Material	Hz Pressure (GPa)	COF ini.	COF end	Wear D on ball (mm)	Wear Width (mm)
65	SWRI	Ni/Ti N2	N2 Ion beam 100 nm*20	Inconel	No	52100	1.3	0.1	0.16		
54	SWRI	Ni/Ti Ar	Ar Ion beam 100 nm*20	Inconel	No	52100	1.3	0.1	0.8	0.41	0.88
56	SWRI	Ni/Ti Ar	Ar Ion beam 2μM	Inconel	No	52100	1.3	0.6	0.6	0.67	0.74
185	SWRI	B4C/Cr	Ar Ion Beam 150/150 nm	Inconel	No	52100	1.1	0.05	0.22	0.21	
186	SWRI	Ti/B4C	N2 Ion Beam 150nm/3μm	Inconel	No	52100	1.1	0.08	0.28	0.25	
187	SWRI	CaF2/Ag	Ar Ion Beam 3 μm	Inconel	No	52100	1.1	0.3	0.2	0.33	
188	SWRI	Ti/B4C	Ar Ion beam 150nm/2μm	Inconel	No	52100	1.1	0.4	0.4	0.53	
189	SWRI	Ni/Ti	N2 Ion Bean 3 μm	Inconel	No	52100	1.1	0.35	0.21		
27	C408	W-W/Zn	300W/300W 50SPR	Inconel	No	52100	1.3	0.1	0.18		
28	C408	W-W/Zn	300W/300W 50SPR	Inconel	No	52100	1.3	0.31	0.31	0.37	0.59
29	C408	W-W/Zn	300W/300W 50SPR	Inconel	300°C 1 Hr	52100	1.3	0.1	0.12	0.21	0.22
58	C411	NiCr/Zn	300W/200W 100SPR	Inconel	No	52100	1.3	0.45	0.45	0.46	0.74
60	C411	NiCr/Zn	300W/200W 100SPR	Inconel	No	WC	3.4	0.25	0.25	0.15	0.25
61	C410	NiCr/Zn	300W/200W 50SPR	Inconel	No	WC	3.4	0.1	0.8	0.88	0.75
208	C477	B4C	2000W 50SPR	52100	No	WC	2.7	0.4	0.18	0.27	0.16
207	C477	B4C	2000W 50SPR	52100	No	52100	1.1	0.55	0.55	0.34	0.21
174	C477	B4C	2000W 50SPR	52100	100°C 1 hr W*	52100	1.1	0.12	0.18		0.3
176	C468	B4C+MoS 2	2000W 50SPR	52100	No	52100	1.1	0.07	0.09	0.26	
178	C480	B4C/Mo	2000W/350W 50SPR	52100	No	52100	1.1	0.45	0.45		
199	C487	B4C/Mo+B N	2000W600W 80 SPR	Inconel	No	WC	2.7	0.1	0.1		
42	C346	Ag/MoS2	40W/600W 180SPR	52100	No	52100	1.3	0.03	0.03	0.15	0.19

* In water

II.7 High Temperature Reciprocating Friction and Wear Tests (SwRI)

SwRI evaluated the friction and wear behavior of several IBAD and multilayer films with the high temperature test rig shown in Figure 5. Radiused pins (~1") made of Inconel were drawn against Inconel and Si_3N_4 coated flats. Tests were conducted at sliding velocities in the range of 10cm/s at room temperature, 400°C and 600°C with applied loads in the range of one N forces. The stroke distance was 2 cm. The tangential force exerted on each pin was monitored using a calibrated eddy current transducer and a data acquisition system operating at a sampling interval of 500 μs. From the tangential force and applied normal forces, coefficients of friction were determined. The width of the wear scar on pin and flat were also measured after each one hour test.

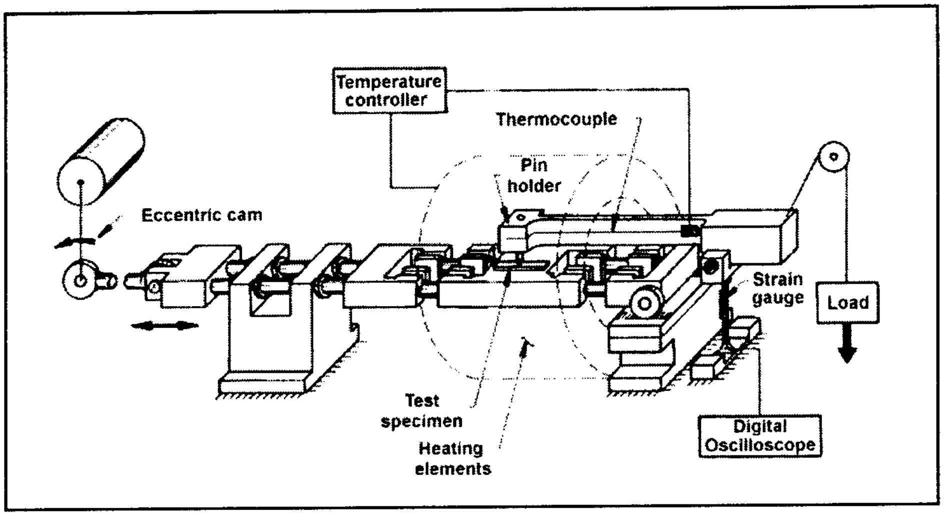

Figure 5. SwRI's high temperature test rig.

The results of these tests are presented in Table 4. Some of these results are also presented graphically in Figure 6.

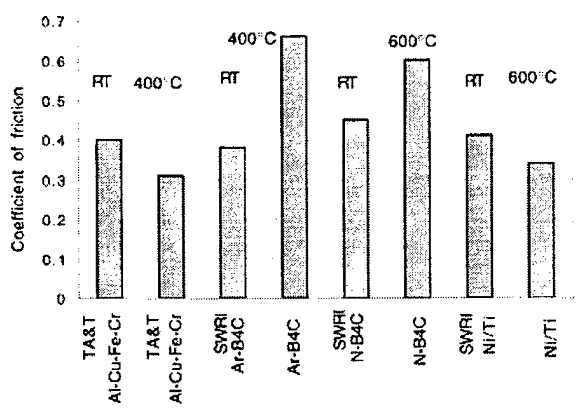

Figure 6. Coefficient of friction of multilayer lubricant films at various isotherms.

Note that the IBAD Ni/Ti exhibited a lower COF at 600°C than it did at room temperature indicating the potential of this system as an adaptive solid lubricant for high temperature use. Post test observation of Ni/Ti wear track after the 600°C test suggested that a self healing process was occurring. Another encouraging result was the extremely low room temperatures COF (0.08) shown by an IBAD B_4C coating that was preannealed in air at 600°C. No TA&T multilayer films were tested at high temperatures at this time except for an AlCuFeCr quasicrystalline film at 400°C. This sample displayed a lower COF at the conclusion of the one hour test suggesting that the formation of a thin lubricious oxide layer was responsible.

Table 4 High Temperature COF Data for IBAD and Magnetron Sputtered Films

Sample/Pin#	μ Initial	μ Final	Pin Scar (in.)	Bar Scar (in.)	Comments
RT runs					
bare CI,#1	0.1	0.44	-	-	-
QSC 448, #2	0.534	0.375	-	-	complete delam
QSC 448 (anneal), #3	0.238	0.568	-	0.028	-
Ar-B_4C, #4	0.55	0.214	-	0.013	best on CI
B_4C/Cr, #5	0.536	0.500	-	-	-
bare Si_3N_4, #6	0.542	0.708	0.030	0.030	-
QSC, #7	0.538	0.530	-	-	-
Ni/Ti, #8	0.487	0.337	0.027	0.015	best on Si_3N_4
N-B_4C, #9	0.437	0.463	0.050	0.038	-
B_4C-Mo, B_4C-Mo	0.204	0.735	-	-	-
400°C runs					
bare Ci, #3	0.424	0.282	0.053	0.062	
QSC 488 (anneal), #1	0.329	0.290	0.060	0.030	
Ar-B_4C, #10	0.650	0.680	0.057	0.039	
600°C runs					
bare Si_3N_4, #9	0.383	0.394	0.075	0.040	
N-B_4C, #8	0.636	0.573	0.033	0.041	
Ni/Ti, #6	0.386	0.304	0.087	0.022	"Self-healing" observed on RT wear track

Although quasicrystalline films were not originally proposed as wide temperature lubricant candidates for this program, deposition of quasicrystalline films under IBAD conditions could be very attractive for the following reason. Under a separate Phase 1 SBIR contract, TA&T developed a breakthrough in target fabrication methods that enable AlCuFeCr and AlCoFeCr quasicrystalline films to be magnetron sputtered. Never before could quasicrystalline films be sputtered from quasicrystalline targets without severe thermal shock induced cracking and fracture.

Now quasicrystalline films can be deposited from any size sputtering target without rapid target disintegration. Therefore, a new vista of practical tribological as well as other thin film quasicrystalline applications are possible. One drawback, however, at least for low temperature substrates is that the as-deposited AlCuFeCr and AlCoFeCr films require annealing at temperatures of 500°C or higher to convert them to the quasicrystalline crystal structure. The use of an ion beam assist while these AlCuFeCr films are being deposited (IBAD conditions) could impart enough energy to the arriving metallic atoms to activate the formation of the quasicrystalline (decagonal or orthrhombic) phases in as-deposited state.

Subsequently, preliminary IBAD experiments were be conducted by SwRI with a quasicrystalline target supplied by TA&T. In addition, magnetron sputtered Zn/W and B_4C/Cr multilayer films were supplied for high temperature tests at SwRI. These films were compared to new IBAD B_4C/Cr and thicker Ni/Ti films deposited and also tested at high temperature by SwRI.

III. ADDITIONAL MAGNETRON SPUTTERING AND IBAD COATING EXPERIMENTS AND FRICTION AND WEAR RESULTS

III.I New Magnetron Sputtered Films

TA&T focused its coating efforts on two principal coating systems during this period of the project. The first multilayer combination was the W-MoS_2 system. Both multilayers and co-sputtered films were deposited. The second area of emphasis was the fabrication of a circular six-inch quasicrystalline target based on the $Al_{79}Cu_7Fe_7Cr_7$ composition. A copper backing plate was also machined for this target to which cold pressed quasicrystalline segments were adhesively bonded with a conductive epoxy. The target was then shipped to SwRI for IBAD trials.

III.2 W-MoS_2 Coatings - Friction and Wear Results

The rationale for examining the W-MoS_2 multilayer and co-sputtered films as potential wide temperature solid lubricants was the likelihood of mixed sulfide-mixed oxide formation. Both MoS_2 and WS_2 are dichalcogenide solid lubricant compounds whose hexagonal basal plane lamellar structure has very weak bonds between the adjacent planes of S atoms. This permits easy shear of the film and associated low friction in a dry sliding mode. Oxidation of MoS_2 becomes significant around 400°C and, over time, forms MoO_3 whose coefficient of friction (COF) is around 0.2 at 700°C. WS_2 is more oxidation resistant, resisting appreciable oxidation until 650°C. The formation of WO_3 together with MoO_3 could well provide reasonable COFs over a broad temperature range. Table 5 depicts four different W-MoS_2 related films and their deposition

characteristics. Two are MoS_2-W cosputtered films (C523 and C526), one is a MoS_2/W multilayer film (C516) and the fourth is a B_4C/W-MoS_2 co-sputtered multilayer film (C529).

Table 5. W-MoS_2 Multilayer and Co-Sputtered Films

Run N0.	Bond Layer	Type Film	Substrate Bias	Chamber Pressure	No. of Revolutions
C516	Ti	MoS_2/W Multilayer	-50W	4mT	300
C523	Ti	MoS_2-W Co-Sputtered	-50W	4mT	500
C526	Ti	MoS_2-W Co-Sputtered	-50W	4mT	500
C529	Ti	MoS_2-W B_4C Multilayer	0	2.5mT	500

Friction and Wear Results Of As-Deposited Films

The COFs were measured using Wear Sciences' ball-on-rotating-disk tester. The coatings were tested under a .5 kg load using a 52100 steel ball and rotation rate of 670 RPM. The test duration was 2250 cycles. These results on the as-deposited films are summarized in Table 6.

Table 6. COFs of As-Deposited W-MoS_2 Multilayered and Co-Sputtered Films

Run N0.	Substrate	Type Film	COF Initial	COF Final
C516	Inconel	MoS_2/W Multilayer	.05	.5
C523	Inconel	MoS_2-W Co-Sputtered	.03	.3
C526	Inconel	MoS_2-W Co-Sputtered	.1	.3
C529	52100	MoS_2-W/B_4C Multilayer	.05	.4

These four films were annealed at 500°C for 16 hours in air to convert them to mixed oxide-sulfide compositions and then retested for friction and wear behavior. These results are presented in Table 7.

Table 7 COFs of 500°C Air Annealed W/MoS_2 & W-MoS_2 Films

Run N0.	Substrate	Type Film	COF Initial	COF Final	Comments
C516	Inconel	MoS_2/W Multilayer	0.7	>1.0	Coating failed stick slip
C523	Inconel	MoS_2-W Co-Sputtered	0.4	1.0	Coating failed several cycles
C526	Inconel	MoS_2-W Co-Sputtered	0.45	>1.0	Coating failed instantly
C529	52100	MoS_2-W/B_4C Multilayer	0.4	0.5	Quite initially

The MoS_2/W multilayer and MoS_2-W co-sputtered films exhibited low room temperature friction coefficients in the as-deposited condition. However, the 500°C annealed samples which were used to simulate chemical reactions that would occur in service at these temperatures yielded

extremely poor room temperature friction and wear results. The W/MoS_2 and MoS_2-W co-sputtered annealed films failed almost immediately, suggesting that the oxidation process destroyed the adhesion of these coatings. Only the B_4C/W-MoS_2 co-sputtered multilayer film (C529) survived the short term friction tests albeit marginal friction coefficients in the 0.4 to 0.5 range. Consequently, no further experimental work was conducted with the W-MoS_2 based sputtered films.

III.3 New IBAD Experimental Films and SwRI Friction and Wear Results

A number of additional IBAD films were deposited on Si_3N_4 substrates. This included a B_4C only film with Ar ion bombardment, a B_4C-Cr multilayer film, two Ni-Ti multilayer films bombarded with Ar and N ions, and a TiC versus Si_3N_4 couple.

The above IBAD films were tested in SwRI's reciprocating pin-on-flat test machine. The TiC pins were machined to a one-inch radius. All tests were conducted for 10-30 minutes using a 1N load and 2 cm stroke at a 3-5 Hz repetition rate. The results of room temperature and 600° tests are presented in Table 8. At room temperature, the initial COFs of the B_4C and N_2^+ Ni-Ti IBAD were below the original goal of 0.2. At the conclusion of the tests, all the films except B_4C exhibited higher CoFs than the base materials.

Table 8. Room and Elevated Friction and Wear Tests of IBAD Films

Sample/Pin#	μ Init	μ Final	Pin Scar (in.)	Bar Scar (in.)	Comments
RT runs (TiC) Bare	.765	.656	.020	.022	
B_4C (Ar IBAD)	.176	.330	.020	.008	
Ni-Ti (Ar IBAD	.690	.661	.015	.022	
Ni-Ti (N IBAD)	.159	.762	.014	.014	
B_4 C-Cr (N IBAD)	.346	.875	.015	.022	
600°Runs Bare	.341	.303	.044	.035	"Whitish" transfer layer
B_4C (Ar IBAD)	1.128	.422	.030	.024	
Ni-Ti (Ar IBAD	.421	.316	.031	.031	
Ni-Ti (N IBAD)	.448	.364	.039	.044	Significant Delamination
B_4 C-Cr (N IBAD)	.432	.366	.049	.039	

The wear scar was markedly less on the B_4C sample and somewhat less on the Ni-Ti (N_2 IBAD) coated Si_3N_4 bar. The Ni-Ti (Ar IBAD) and B_4C-Cr multilayer film showed no improvement in wear resistance compared to baseline TiC-Si_3N_4 materials.

The results of the 600°C tests were surprising. The COFs of all the samples were higher than the bare baseline couple. A whitish transfer layer was observed with the TiC-Si_3N_4 bare couple suggesting that the formation of TiO_2 may have contributed to the two-fold reduction in COF compared to its room temperature values.

The high COFs obtained with Ni-Ti Films were especially puzzling given the previous SwRI experimental results with Ni-Ti samples that showed low COFs at 800°C. It is possible that 600°C is too low a temperature to form lubricious complex oxides. The other possibility is that this combination only exhibits low COF at very high temperatures.

III.4 Final Set Of Deposition Experiments

AlCuFeCr samples (C454) on Inconel substrates were shipped to SwRI for room-and elevated temperature friction and wear measurements on SwRI's reciprocating pin-on-flat tester. IBAD noble metal coatings of Pt and Au/Cr were also deposited on Inconel substrates and tested at high temperatures. In addition, a special circular AlCuFeCr quasicrystalline target was subjected to dual sputtering - IBAD experiments at SwRI.

III.5 SwRI Room and High Temperature Friction and Wear Results

The friction and wear results from the SwRI room and high temperature tests are presented in Table 9.

Table 9. Room and Elevated Temperature Friction and Wear Data

Coating	PIN	FLAT	T°C	μ in	μ final	Pin Scar (in)	Bar Scar (in)
AD QC454	Inco	Inco	25°C	1.06	.875	-High	Wear
AD QC454	Inco	Inco	500°C	0.38	0.56	High	Wear
AN QC454	Inco	Inco	25°C	0.68	0.81	0.06	0.014
AN QC454	Inco	Inco	350°C	0.37	0.44	0.07	0.048
Pt	Inco	Inco	25°C	0.18	0.49	0.01	0.009
Pt	Inco	Inco	500°C	0.74	0.59	0.08	0.049
Au-Cr	Inco	Inco	25°C	0.50	0.32	0.01	0.013
Au-Cr	Inco	Inco	500°C	0.91	0.64	0.11	0.035

As expected the as-deposited (AD) AlCuFeCr quasicrystalline coating from sputtering run 454 exhibited unusually high friction and wear at room temperature. In the 500°C test, the initial and final friction values dropped significantly suggesting that the amorphous AlCuFeCr film had begun

to convert to a quasicrystalline structure. The friction coefficients and wear of the annealed (AN) 454 samples were significantly lower than the as deposited AlCuFeCr film. Again the μ in and μ f values were measurably lower at elevated temperature (350°C) than the room temperature COFs. A AlCuFeCr IBAD sample that was sputtered at 5 x 10^{-6} Torr and ion implanted with 6 KeV Ar at 80W and 20 ma was shipped to TA&T for annealing and room temperature friction and were measurements. A stylus profilometer trace (Figure 7) revealed that this film was 1.2μm thick.

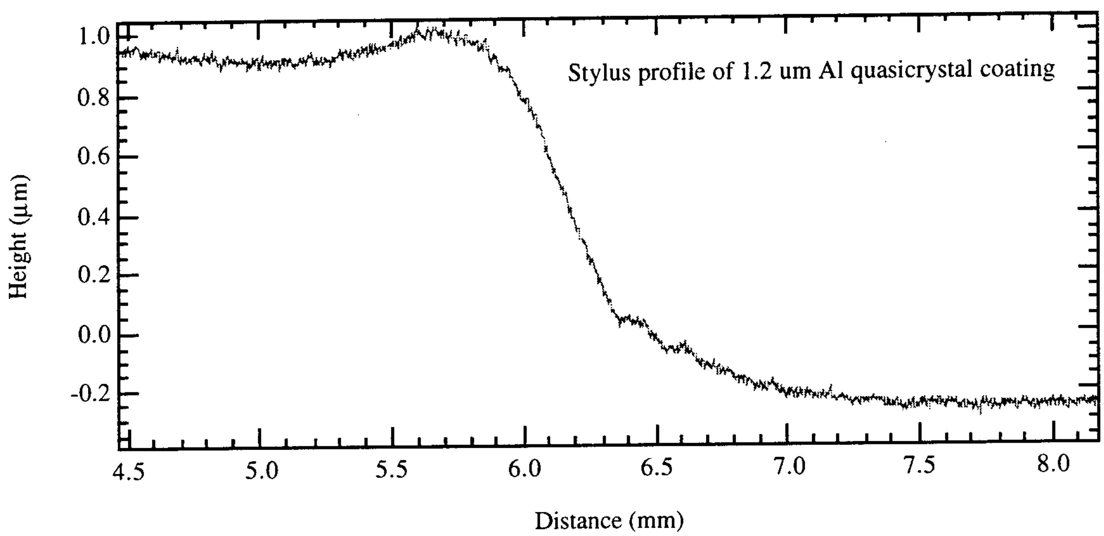

Figure 7. Stylus profilometer trace of IBAD AlCuFeCr film.

The IBAD AlCuFeCr film was annealed for 16 hours at 700°C in air. The peaks from the subsequent X-ray diffraction pattern did not, however, match those of the AlCuFeCr quasicrystalline phases. The annealed sample was subjected to a room temperature friction and wear test at 670 RPM, 0.5 kg load under a 52100 steel ball. Even though the film was not quasicrystalline structure, it exhibited constant, although high COF (0.6).

IV. BALL BEARING FIXTURING AND COATING EXPERIMENTS

In Phase I, TA&T designed, built and evaluated special fixtures for coating ball bearing races and balls. The fixturing for coating the outer race enabled the race to be canted (tilted) at a 30° angle from the horizontal to permit line of sight access for the impinging coating atoms while the race was being rotated. No special fixturing was required for the inner race.

The fixturing for coating balls in the Sloan Model 1800 system with wall mounted vertical targets was a challenging problem. Normally, bearing balls are coated with horizontally mounted targets that sputter downward onto balls that roll randomly in a rotating shallow dish-like fixture.

After several design iterations, a cage structure in which the balls were placed was designed and constructed as in Figure 8. The restraining bars of the cage were very thin so they would not block the coating flux from the target as the balls rotate in a random fashion. This design proved to be very successful as depicted in the photograph shown in Figure 9. Dense, high-gloss sputtered coatings were also successfully deposited on the outer and inner races as shown in Figures 10. These MoS_2 multilayer coated bearings were shipped to Sundstrand Aerospace for high temperature tests.

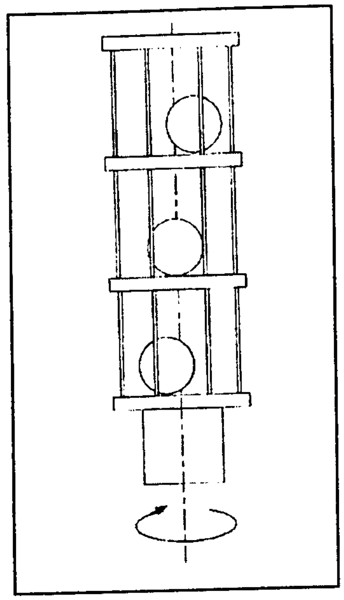

Figure 8 Rotating cage fixture for uniform coating of bearing balls.

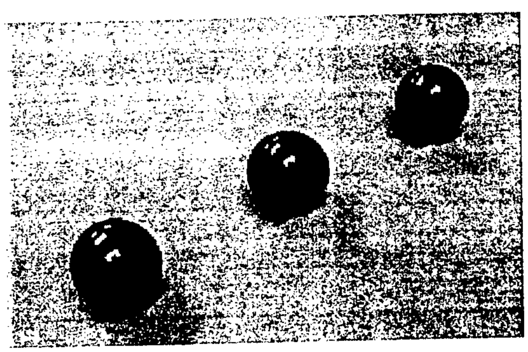

Figure 9 Solid lubricant sputtered coated balls from cage fixture.

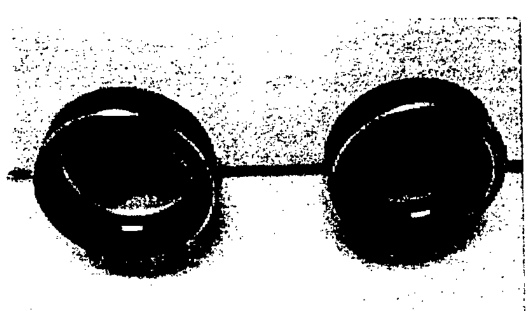

Figure 10 Solid lubricant sputtered coated outer races from tilted fixture

Additional fixturing was built and used for coating 400 Si_3N_4 balls for Revolve Magnetic Bearing Co. of Calgary, Canada. These balls will be used in back-up ball bearings for magnetic suspended shafts. It is not desirable to use oil or grease lubrication because of potential volatilization and migration problems. Therefore, MoS_2 sputtered coatings are ideal. These coated balls are currently under test in bearing rigs. Successful performance will likely result in a niche commercial market.

V. CONCLUSIONS

Of all the magnetron sputtered and IBAD coatings that were evaluated as wide temperature range solid lubricants, only the AlCuFeCr quasicrystalline samples exhibited enough promise to recommend further investigation. A phase II effort should concentrate on the developing deposition protocols, stoichiometries and annealing treatments for AlCuFeCr and AlCoFeCr systems that produce optimum friction and wear properties from room temperature to 800°C.